FIELD AND LABORATORY EVALUATION OF DEGRADATION, LEACHING, STABILITY IN STORAGE AND BIOAVAILABILITY OF SOIL TERMITICIDES ON THE ASIAN SUBTERRANEAN TERMITES, *Coptotermes gestroi* (BLATTODEA: RHINOTERMITIDAE)

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by

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TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS

ºC	Degree Celcius
%	Percentage
/	Per
cm	Centimeter
g	Gram
ml	Milliliter
mm	Millimeter
ppm	Parts per million
RH	Relative humidity
LT_{50}	Lethal time required to kill 50% of population exposed
LT_{95}	Lethal time required to kill 95% of population exposed
±	Central range
>	More than
<	Less than
RT	Retention time
EPA	US Environmental Protection Agency
d	Days
HPLC	High performance liquid chromatography
UPLC	Ultra-high Performance Liquid Chromatography
P	Significant
ACN	Acetonitrile
ANOVA	Analysis of variance
USDA	United States Department of Agriculture
n	Number of samples

LIST OF APPENDICES

PENILAIAN LAPANGAN DAN MAKMAL KADAR DEGRADASI, KEUTUHAN, LARUT RESAP DAN KETERSEDIAAN BIOLOGI TERMITISID TANAH TERHADAP ANAI-ANAI SUBTERRANEAN *Coptotermes gestroi* (BLATTODEA: RHINOTERMITIDAE)

ABSTRAK

Rawatan termitisid tanah adalah kaedah asas untuk mengawal populasi dan serangan anai-anai dengan mewujudkan halangan berterusan di sekeliling struktur. Walau bagaimanapun, termitisid berkemungkinan menghilang bergantung kepada separuh hayat, kadar degradasi, aktiviti larut lesap dan kaedah penyimpanan. Dalam kajian ini, kadar degradasi dan separuh hayat tiga termitisid iaitu Maxxthor 100 SC (bifenthrin), Chalcid 5.0 SC (fipronil) dan Prothor 200 SC (imidacloprid) ditentukan di lapangan dan di makmal. Kajian lapangan dijalankan dengan kaedah penggalian dan rawatan pembetulan tanah. Fipronil menunjukkan termitisid yang paling utuh di lapangan kerana mempunyai kadar penurunan yang lebih rendah (atas= 4.19 ppm/hari; bawah= 4.06 ppm/hari) dan separuh hayat yang lebih tinggi (atas = 267.99 hari; bawah= 282.56 hari). Manakala, imidacloprid mempunyai kadar degradasi tertinggi (atas= 6.87 hari; bawah= 6.87 hari) dan kadar separuh hayat lebih rendah (atas= 32.25 hari; bawah= 32.35 hari). Kajian makmal mengenai degradasi termitisid menunjukkan bahawa bifenthrin lebih utuh di dalam tanah berbanding fipronil dan imidacloprid. Ujian ketersediaan biologi kepada *Coptotermes gestroi* [Wasmann] menunjukkan bifenthrin mempunyai nilai terendah untuk LT_{50} (atas= 7.114 jam; bawah= 4.966 jam) dan LT_{95} (atas= 37.121 jam; bawah= 21.243 jam) di lapangan dan di dalam kajian

makmal (purata LT_{50}= 21.119 jam; LT_{95}= 38.454 jam). Aktiviti pelunturan termitisid menggunakan kaedah kolum tanah menunjukkan bifenthrin mempunyai sifat peyerapan yang baik kerana mempunyai kepekatan yang lebih tinggi di bahagian atas kolum (Lempung berpasir = 892.77 ppm; Pasir berlempung= 1060.93 ppm) berbanding fipronil dan imidacloprid. Tiada perbezaan signifikan di antara tanah (F= 2.355; df= 1; P= 0.131) tetapi terdapat perbezaan signifikan antara termitisid (F= 265.94; df= 2; P= 0.00). Semua termitisid menunjukkan kadar degradasi yang tinggi yang mana imidacloprid menunjukkan nilai separuh hayat tertinggi (9.42 hari) dan kadar degradasi terendah (29.66 ppm /hari). Keputusan menunjukkan perbezaan yang signifikan di dalam termitisid yang diuji (F= 154.112, df= 2, P= 0). Imidacloprid menunjukkan kepekatan lebih tinggi (111.97 ppm) selepas 30 hari di dalam larutan cecair berbanding fipronil dan bifenthrin. Warna botol (F= 0.181, df: 1, P= 0.672) dan tempat penyimpanan (F= 5.495, df= 1, P= 0.977) tidak memberi kesan signifikan terhadap kepekatan termitisid selepas 30 hari. Berdasarkan kajian ini, fipronil dan bifenthrin disyorkan sebagai rawatan termitisid tanah kerana mempunyai nilai separuh hayat yang tinggi dan kadar degradasi yang rendah. Bifenthrin adalah termitisid yang paling sesuai digunakan semasa musim hujan kerana keupayaannya yang baik untuk melekat pada zarah tanah. Dengan menggunakan bifenthrin, bangunan dilindungi dengan baik daripada serangan anai-anai dan pada masa sama, selamat untuk persekitaran. Adalah juga disyorkan bahawa termitisid perlu digunakan segera selepas pencampuran kerana semua termitisid diuji memperlihatkan kadar degradasi yang tinggi di dalam tempoh 14 hari.

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ABSTRACT

Soil termiticide treatment is a fundamental method to control termite population and infestation by creating a continuous barrier surrounding the structures. However, termiticides may dissipate, depending on a half-life, a degradation rate, a leaching activity and a storage method. In this study, the degradation rate and half-life of three commercially available termiticides, namely Maxxthor 100 SC (bifenthrin), Chalcid 5.0 SC (fipronil) and Prothor 200 SC (imidacloprid) were determined under the field and laboratory conditions. Fipronil showed the most persistent termiticide in the field study as it had a lower degradation rate (top= 4.19 ppm/day; bottom= 4.06 ppm/day) and a higher half-life (top= 267.99 days; bottom= 282.56 days). While, imidacloprid had the highest degradation rate (top= 6.87 ppm/day; bottom= 6.87 ppm/day) and a lower half-life (top= 32.25 days; bottom= 32.25 days). The laboratory study on termiticide degradation indicated that bifenthrin was more persistent in the soils compared to fipronil and imidacloprid. The bioavailability test on *Coptotermes gestroi* [Wasmann] showed that bifenthrin had the lowest values of LT_{50} (top= 7.114 hours; bottom= 4.966 hours) and LT_{95} (top= 37.121 hours; bottom= 21.243 hours) in the field study as well as in the laboratory study (average LT_{50}= 21.119 hours; LT_{95}= 38.454 hours). Leaching activity of the termiticides using a soil column method revealed that bifenthrin had a good adsorption characteristic as it noted a higher concentration at the top of the column (Sandy loam= 892.77 ppm; Loamy sand= 1060.93 ppm) compared to fipronil and imidacloprid. There was no significant difference between soil types (F= 2.355; df= 1; P= 0.131) but, there was a significant difference between termiticides used (F= 265.94; df= 2; P= 0.00). All termiticides showed a high degradation rate. Imidacloprid showed the lowest degradation rate (29.66 ppm/day) and the highest half-life (9.42 days). The result also indicated that there was a significant difference in termiticides tested (F= 154.112, df= 2, P= 0). Imidacloprid indicated a higher concentration (111.97 ppm) after 30 days in aqueous solution compared to fipronil and bifenthrin. Bottle colours (F: 0.181, df= 1, P= 0.672) and storage places (F= 5.495, df= 1, P= 0.977) did not significantly affect the concentration of termiticides after 30 days. Based on this study, fipronil and bifenthrin are recommended in soil termiticide treatment due to their high half-life values and low degradation rate. Bifenthrin is the most suitable termiticide to be used during a raining season due to its profound ability to adsorb to the soil particle. By using bifenthrin, the building is well-protected from termite infestation and at the same time, is safe for the environment. It is also recommended that termiticides should be immediately used after mixing as all termiticide exhibited a high degradation rate within 14 days.

CHAPTER 1

GENERAL INTRODUCTION

Termites are highly destructive polyphagous insect pests, which largely damage household materials, finished goods, plant and agricultural crops such as sugarcane, millet, barley and rice (Upadhyay et al., 2010). Among 3106 termites species identified, 363 species are considered as invasive (Krishna, et al., 2013) Globally, termite infestation caused between US $ 22 billion to US $ 40 billion in property damages worldwide (Rust & Su, 2012) and approximately US $ 400 million per year in Southeast Asia (Lee, 2007). Subterranean termites attack included 90% of total economic loss and 70% of construction damages (Kuswanto et al., 2015). In Malaysia and Singapore, 12 species of subterranean termites from seven genera (*Coptotermes, Macrotermes, Microtermes, Globitermes, Odontotermes, Schedorhinotermes*, and *Microcerotermes*) can be readily found in and around building and structure (Lee et al., 2007). Subterranean termites in the genus *Coptotermes* sp. are structural pests that have become globally distributed beyond their native range in Southeast Asia. Based on estimation data in 2010, cost of damages by termites up to $40 billion annually worldwide (Rust & Su, 2012).

After World War II, cyclodienes have been recognised as highly effective termiticides (Ware, 2000). From the late 1940s until 1988 cyclodienes have been used as pre-construction soil treatment for controlling subterranean termites (Lewis, 1980; Su & Scheffrahn, 1990). Chlordane, one of the termiticides belong to the group cyclodienes was extremely effective and highly stable in soil. These advantages made chlordane a preferable termiticide to control termites, hence, was extensively used for several decades (Grace, et al., 1993; Su & Scheffrahn, 1990). However, due to its long persistence in the soil, questions were raised concerning the effects of chlordane to the environment (Lewis, 1980; Su & Scheffrahn, 1990; Wood & Pearce, 1991). High toxicity and capability to bio-accumulate in foods have resulted in the banning of chlordane and other related chemicals in most of the countries in the 1970s and 1980s (Iwata, et al., 1993; Ntow, 2005; Ware, 2000; Xue, et al., 2006).

After banded of cyclodienes two groups of termiticides are generally available, namely chlorpyrifos, organophosphate-based termiticides and pyrethroids. The persistent of chlorpyrifos is significantly shorter compared to cyclodienes. (Grace et al., 1993; Lenz et al., 1990). Unfortunately, the U.S. Environmental Protection Agency (EPA) revised chlorpyrifos risk assessment in 2000 and cancelled the usage of chlorpyrifos (EPA, 2000). As a result, pyrethroids are the main chemical termiticides used for controlling subterranean termites. Pyrethroids are more persistent than chlorpyrifos, but less stable in soil compared to previously banned cyclodienes (Lenz et al., 1990; Pawson & Gold, 1996; Su & Scheffrahn, 1990).

In 2000, several new non-repellent soil termiticides were introduced in the market: imidacloprid, a chloronicotinyl by Bayer Corporation at 2000, fipronil, a phenyl pyrazole by Aventis Corporation at 2001, and chlorfenapyr, a pyrrole by BASF Corporation at 2001 (Wiltz, 2012). Non-repellent termiticides are the improved formula of the pyrethroids because subterranean termites unable to detect gaps in the treatment (Potter & Hillery, 2002).

Roughly, 6000000 chemical compounds have been produced with 1000 new products are made annually. Among these, between 60000 and 95000 chemicals are commercially used (Ortiz-hernández, et al., 2013). Malaysia and most of the Southeast Asian countries rely heavily on the use of soil termiticides against subterranean termites in urban environments (Lee, 2002). However, extensive use of pesticides would lead to environmental pollution. The use of pesticides in large amount does not entirely meet the objectives of its application due to several drawbacks such as degradation, volatilisation and leaching (Chai, et al., 2013; Ismail & Kalithasan, 2003).

At present, many countries particularly Asian countries preferred a method or a chemical-based termiticide that are safe for the environment. A tremendous amount of research in recent years has been focusing on termite control technologies to reduce environmental contamination and the risk to human health. Thus, a fate of termiticides such as the persistence, leaching and storage procedures should be determined beforehand.

Studies on degradation, leaching and storage of bifenthrin, fipronil and imidacloprid have been investigated by many researchers throughout the world, but, these subject areas have not been done in Malaysia. Therefore, the objectives of this study were:

Objective 1 (Chapter 3): Determination of degradation rate, half-life, and bioavailability of bifenthrin, fipronil and imidacloprid under field and laboratory conditions

1. To evaluate a degradation rate and half-life of bifenthrin, fipronil and imidacloprid under field conditions,
2. To determine a degradation rate and half-life of bifenthrin, fipronil, imidacloprid in different soils (Sandy loam and Loamy sand) and at different temperatures (30°C and 40°C),
3. To determine LT_{50} and LT_{95} values (lethal time for 50% and 95% termite mortality) of termiticides in no-choice assay.

Objective 2 (Chapter 4): Leaching of termiticides (bifenthrin, fipronil and imidacloprid) in different types of soils under laboratory conditions

1. To evaluate the leaching of termiticides (bifenthrin, fipronil and imidacloprid),
2. To determine the leaching of termiticide in different soils (Sandy loam and Loamy sand).

Objective 3 (Chapter 5): Evaluation of optimum conditions for termiticide storage

1. To evaluate the stability of termiticides (bifenthrin, fipronil and imidacloprid) in aqueous solution,

2. To determine termiticide residuals in different bottle colours (black and white),
3. To determine the stability of termiticides stored in different places (an idle car and a chemical store).

CHAPTER 2

LITERATURE REVIEW

2.1 A brief introduction to termites

Termites are living organisms that play an important role in tropical ecosystems. They mainly feed on a variety of organic detritus such as decaying leaves, dry grasses, humus, animal dungs and living or dead woods (Brossard et al., 2007; Kuswanto et al., 2015). These so-called ecosystem engineers have a major influence on plant decomposition, soil structure, carbon mineralisation, nutrient availability and the catalyst for microbial activities (de Bruyn & Conacher, 1990; Lavelle et al., 1997; Dawes, 2010; Muvengwi et al., 2017). Some of them, too, are capable of influencing the plant growth (Gillison et al., 2003; Donovan et al., 2007).

Termites are generally soft-bodied, pale in colour and possess a mouth part for chewing, biting and consume cellulose as a food source (Verma et al., 2009). They have three segments, namely head, thorax and abdomen, of which the thorax has a broad joining to the abdomen that resembles a wide waist (Grimaldi & Engel, 2005). Termites are known to undergo an incomplete metamorphosis with three stages; egg, nymph and adult stages (Prahlad & Chimkod, 2012).

Termites live in a very complex colony, ranging from several hundred to several million-individual caste at maturity colony levels. The colony consists of nymph alates, reproductive females and males, sterile workers and soldiers (Eggleton, 2000; Wako, 2015). The workers establish the major proportion with 47.77% from the total individuals, followed by larvae (39.99%), soldiers (15.37%) and pre-soldiers (0.77%) (Lee & Lee, 2011). Each colony has a set ratio for workers, soldiers and nymphs, where, to achieve a balanced set ratio, the colony members will be restored from developing nymphs if any colony members are lost or die (Wako, 2015). An unbalanced set ratio causes an increased burden to the colony, for example, excessive number of soldiers leads to excessive work to the workers in order to sufficiently feed the caste (Kuswanto et al., 2015).

Termite caste can be divided into two categories of individuals; fertile (reproductive) and sterile individuals (Roisin, 2000). The sterile caste consists of workers, pre-soldiers and soldiers, while, fertile are alates (primary reproductive caste) and neotenics (secondary reproductive caste) (Watanabe et al., 2014). Termite workers and soldiers are wingless and eyes-lacking (Lee & Neoh, 2014). Morphologically, the soldiers are larger than the workers with an enlarged head and true jaw known as a mandible capable of ejecting liquids (Verma et al., 2009; Prahlad & Chimkod, 2012). Most of the work in the colony are performed by worker caste including feeding the other caste, making tunnels, grooming the nest-mates and excavating the nests (Lee & Neoh, 2014). While, the soldier caste responsible for colony defence and guarding its occupants from enemies and outsiders (Ghaly & Edwards, 2011). From nympal stages, alates or primary reproductives (king and queen) are equipped with well-developed wings, ovaries and testes for reproduction purposes where the queen could lay approximately thousands of eggs a day through the abdomen (Verma et al., 2009; Prahlad & Chimkod, 2012; Watanabe et al., 2014). Meanwhile, secondary reproductives act as substitutes when the queen dies or too old to lay eggs (Lee & Neoh, 2014).

During the swarming season, the alates fly a few hundred meters away to find a suitable nesting area and form a new colony (Ghaly & Edwards, 2011). According to Lee & Neoh (2014), the alates are able to fly as height as 15 m with a distance of

200 to 300 meters. The size of the male alates would decrease, while, on the other hand, the size of female alates would increase tremendously (Wagner et al., 2008). The female alates (queens) start to lay yellowish-white eggs that would hatch after 50 to 60 days (Wako, 2015). The hatched eggs are then termed as larvae. Due to their incomplete and soft mouth part, the larvae are initially fed by the king and queen until they are able to self-feeding (Lee & Neoh, 2014). The newly-formed workers would resume the feeding job by collecting the food, enlarging the nest and taking care of the eggs and the young larvae (Ghaly & Edwards, 2011; Lee & Neoh, 2014). Nymphs would be produced and developed into either neotenic reproductives or alates only when the colony reaches its maturity and the foods are abundant (Vargo & Husseneder, 2009; Lee & Neoh, 2014). Soldiers are formed from worker instars, pseudorgated or apterous immature forms (Casarin, et al., 2008). However, unlike other caster, soldiers are unable to molt (Lee & Neoh, 2014)

2.1.1 Classification of Termites

Termites are generally classified according to their feeding behaviour and habitat (Nalepa, 1994; Lee & Neoh, 2014). They can be categorised into three groups: drywood, dampwood and subterranean termites. The drywood termites are often found inside the drywood, such as structural timber of buildings (Verma et al., 2009). The main drywood termite pests (Kalotermitidae) that belong to the genus *Cryptotermes* are considered as serious pests (Rust & Su, 2012). They are less dependent on moisture and soil to survive compared to other termite groups. Usually, their faecal pellets are one of the early signs of timber infestation (Lee & Neoh, 2014). Thousands of individuals of drywood termites could colonise and live in a piece of wood when the infestation occurs (Rust & Su, 2012). Contrasting to drywood termites, the dampwood termites feed on rotten woods, wet and old tree stumps and buried timbers (Lacey et al., 2010; Lee & Neoh, 2014). Their nest is made up of insulating materials like woods and soils that provide protection to their colony (Lacey et al., 2010). While, subterranean termites are completely nested under the ground as they highly depend on a soil moisture. They are, however, connected to the food sources through mud galleries (Lee & Neoh, 2014; Theraulaz et al., 2003). The subterranean termites also extraordinarily exist in a huge number of individuals per colony and are the most economically-destructive group worldwide (Lee & Neoh, 2014).

2.1.2 Importance of Termites

Termites are important in decomposition and nutrient cycling (Collins, 1981; Holt & Coventry, 1988). They help in breaking down any fallen trees and other cellulose-based materials in the forest. They also provide foods for other insects and animals. Anderson et al. (2010) and Owen-Smith (2002) reported that herbivores have high tendency to forage on selecting patches (termites' mound) with abundance of nutrition and lower predation risk.

Termite mounds are important to ecosystems. According to Yamashina (2014), termite mounds support the woody plant assemblages (Loveridge & Moe, 2004; Traoré et al., 2008) and herbaceous layers (Okullo & Moe, 2012). The vegetation communities turn the mounds as foraging hotspots with a diverse range of consumers (Levick et al., 2010; Loveridge & Moe, 2004). The epigeal termite mound contains a tremendous amount of nutrients and high level of soil moisture, thus, benefiting plants and other surrounding living organisms (Traoré et al., 2008; Moe et al., 2009; Davies et al., 2014). The uniqueness of huge termite's mound has also become an attraction in tourism industries for some countries. In Southeast Asia, a worship on termite mound is common, of which, local people believe that termite mound or better known as 'Keramat' in Malay was created by a spirit to ensure the safety and continuous prosperity (Lee & Neoh, 2014).

In traditional medicine perspectives, eating the queen could allegedly cure various diseases such as aphrodisiac, asthma and lung-related diseases. The termite mound is also consumed by local people in certain African regions as they believe that minerals in the termite mound are essential for malnourished children, lactating mothers and pregnant women (Lee & Neoh, 2014).

2.1.3 Economically Important Termites

According to Krishna et al., (2013), 3106 living and fosil species of termites recorded and 363 termite species significant pest insects. Among the subterranean termites, the genus *Coptotermes* contributes to the largest number of species, followed by the genera *Macrotermes*, *Reticulitermes* and *Odototermes* (Rust & Su, 2012). Damages caused by termites are approximately US $ 22 billion to US $ 40 billion worldwide (Su, 2002; Rust & Su, 2012), whereas, damages caused by subterranean termites alone are approximately US $ 400 million per year (Lee, 2007).

The most common species in Malaysia and Singapore are those in the genus *Coptotermes* (84.1%), followed by *Macrotermes gilvus* (6.0%) and *Schedorhinotermes medioobscurus* (3.8%) (Lee et al., 2003). Subterranean termites in the genus *Coptotermes* are structural pests that cause a serious damage to buildings and structures and have become globally distributed beyond their native range in Southeast Asia. It it reported that *Coptotermes gestroi* species is the most aggressive in attacking the urban structures and buildings (Kirton & Brown, 2003).

Subterranean termite infestation usually begins from the nest under the ground. Then, they build one or more galleries (mud tubes) on trees or building walls to reach for food sources (cellulose). They, however, remain connected to the ground to obtain the moisture from the soils and come back forth to the centre nest (Ghaly & Edwards, 2011). Subterranean termites mainly attack the buildings located in areas formerly used for plantations and forested lands (Mo et al., 2006). Anthropogenic activities such as deforestation areas or plantations for human settlement are often left with piles of litter scattered on or in the ground. Thus, the residential areas already provide an abundant amount of food sources for termites. Rich and readily available food sources have made the eradication of termite infestation to be more challenging and nearly impossible, which simultaneously causes a huge loss to both plant and human structures (Verma et al., 2009).

2.1.4 Coptotermes gestroi

Kingdom	: Animalia
Family	: Rhinotermitidae
Genus	: *Coptotermes*
Scientific name	: *Coptotermes gestroi* [Wasmann]

Coptotermes gestroi [Wasmann] is an important pest that frequently found in tropical regions (Li et al., 2009). The species is invasive and is known to be endemic in Southeast Asian countries including Malaysia, the Philippines, Indonesia and Singapore (Li et al., 2009). Termites are able to spread far beyond their native ranges due to human activities. It was previously collected in Marquesas Islands (Pacific Ocean), Mauritius and Reunion (Indian Ocean) in the early 1930s to 1950s (Scheffrahn & Su, 2008). The species was then reported for the first time in the United States in

1996 (Su et al., 1997). A recent collection shows that this species keep on spreading throughout the world (Scheffrahn & Su, 2008).

Members of this species are found to be infested the buildings in urban, rural or suburban areas (Kirton & Azmi, 2005) and are highly adaptable to human environments where settlements prevail and attacks mainly cellulose-based structures such as parquet floors, cabinets, roofs windows and door frames. They build a secondary nest that connects directly to the main nest (Janei & Costa-Leonardo, 2015). The main nest is where the king and queen live, while, the secondary nest is established for the growth of the colony. The colony is hugely dominated by workers, while soldiers are responsible to protect the colony (Janei & Costa-Leonardo, 2015).

2.2 Termite control and management

A myriad of approaches has been used to control and eliminate the termites-chemically, physically and biologically. For over the years, a chemical pesticide (termiticide) is the most common and widely used in termite control and management. However, other methods are also applicable and have been extensively studied by researchers to suppress the termite populations e.g. toxic baits, stainless steel mesh (Termimesh) and a barrier technology with inert granitegard (Su, 2002; Wege et al., 2003; Su et al., 2004).

Physical barrier firstly reported by Ebeling & Pence, (1957) by using uniform size sand particles. Then, the continuous horizontal barrier using 2.00 to 2.80 mm single-sized particle barrier during pre-construction installation is considered as the most effective means in providing the building structure a protection (Su et al., 1992). A decade later, O'Toole et al., (2003) indicated that termites were incapable to penetrate a 0.66 x 0.45 mm fine stainless-steel mesh hole. A biological control such as using entomopathogenic micro-organisms has a great advantage over another form of termite control such as free from environmental contamination and is safe for non-target organisms (beneficial insects and animals for ecosystem) (Kaya & Gaugler, 1993). However, this control method is not field-proven and merely works under laboratory conditions with a limited number of termites in specific environments (Kuswanto et al., 2015).

There are two common approaches used to control subterranean termites: creating a chemical barrier using termiticides in the soil and baiting system for managing subterranean termite populations around or near the structure (Su, 2011). The baiting system is recently gaining its popularity. The principle of termite baiting system is introducing the termites with baits containing an active ingredient in the station. The active ingredient is a chitin synthesis inhibitor that causes molting metabolic disorder where termites would fail to form a chitin and subsequently die. At first, termites begin to forage in the station, then they would bring along the active ingredient to their nest to feed the occupants. This method has been proven to effectively reduce the pesticide contamination to the environment (Verkerk & Bravery, 2000; Potter, et al., 2001).

Soil treatments have been widely used in the early 1990s. However, research on termiticides (pesticides used to control termites) was firstly reported in the early 1950s (Scheffrahn et al., (1997). Termiticides are typically used for covering the parameter of the building foundation to protect the structure from subterranean termite infestation. Initially, the soil treatments are believed to eradicate the termite populations, however, the treatments only serve as foraging barriers between sources of infestation (termites nest) and the protected structures (Randall & Doody, 1934; Nan Yao Su, 2011).

Among termiticides used in the 1930s to 1950s were sodium arsenite, DDT, trichlorobenzene, creosote, pentachlorophenol, and ethylene dibromide (Su, 2011). The use of cyclodienes (chlordane, heptachlor, aldrin, and dieldrin) was widespread until the mid-1980s and was later cancelled due to an agreement in 2000 between registrants and the United States Environmental Protection Agency (USEPA) (Su, 2011). Other termiticides such as bifenthrin, permethrin, chlorfenapyr, cypermethrin, fipronil and imidacloprid have also been used to control the termite activity (Su & Scheffrahn, 1990).

The cyclodienes were soon replaced by organophosphate and pyrethroid, however, the use of chlopyrifos (organophosphate group) was prohibited in 2006 based on an agreement in 2000 between registrants and the USEPA. Currently, the termiticides used in soil treatments are either repellent termiticides (cypermethrin, bifenthrin and permethrin) or non-repellent termiticides (imidacloprid, chlorantraniliprole, fipronil and chlorfenapyr) (Su, 2011).

In Malaysia, the control strategies against subterranean termite rely on soil termiticides (termiticides) (Chung & Lee, 1999). Basically, soil termiticide treatments can be divided into pre- and post-constructions. A total of 62% of the soil treatments are used for post-construction on the building, while 48% are used for pre-construction. The post-construction treatment includes utilising trenching, dusting and corrective soil treatment. The treatment is somewhat popular among major pest control companies in Malaysia, where almost 50% of the total post-construction use a corrective soil treatment and dusting (Lee, 2002).

2.3 Classes of termiticides

Pyrethroids are synthetic termiticides mainly designed based on pyrethrin derived from chrysanthemum species (Ray, 1991; Feo et al., 2010) The mortality rate is extremely high even at low doses *via* a direct contact. Pyrethroids attack the target insect's nervous system and severely impair its coordinate movement (Koehler et al., 2011). It also has a lower mammalian toxicity, lower environmental persistence and selective termiticide activity (Hill, 1989; Feo et al., 2010). Permethrin, cypermethrin, bifenthrin and deltamethrin, to name a few, are several formulated pyrethroids available in the market (Ashaari et al., 2008). Synthetic pyrethroids have been widely commercialised for insect and animal pest control either in agricultural sectors or in households. The use of synthetic pyrethroids in the United States sharply increased following the ban of organophosphate products (diazinon and chlorpyrifos) for certain uses (Hill, 1989). Synthetic pyrethroids are known for their poor mobility in the soils due to the ability to strongly bind to soils and sediments (Hill, 1989; Kabashima et al., 2004; Weston et al., 2009; Ding et al., 2010; Weston & Lydy, 2010).

According to Soderlund (2012), pyrethroids have been used in pest control and management for 30 years. Other resources stated that pyrethroids are widely used since the 1970s to control insect pests in public health and agriculture. In the USA, the use of pyrethroids is continuously increasing up to 23% by the mid-1990s (Casida & Quistad, 1998).

The phenylpyrazoles are newly developed chemicals with herbicidal and insecticidal properties (Yanase & Andoh, 1989; Klis et al., 1991). Fipronil is one of the common phenylpyrazole termiticides that can be transformed into toxic metabolites fipronil sulfone and fipronil sulphide (Brennan et al., 2009). Phenylpyrazoles have a broad spectrum of insecticidal activities, controlling pests on various crops such as rice and cotton, fleas and ticks on domestic animals, locusts, grasshoppers, cockroaches and ants. These pesticides also have lower mammalian toxicity, lower environmental persistence and selective termiticide activity (Hainzl et al., 1998; Feo et al., 2010).

Neonicotinoids are the most significant chemical class of termiticides after synthetic pyrethroids being introduced. Nowadays, more than 120 countries have used neonicotinoids for controlling several insect pests such as whiteflies, plant- and leaf-hoppers, aphids, beetles and termites. The use of these termiticides are not restricted to destructive insect pest in agriculture only but are also applicable in veterinary medicine and urban entomology. The mode of action of neonicotinoids is through the central nervous of insects, causing nerve excitation and paralysis which eventually lead to death (Fishel, 2016). Imidacloprid is one of the neonicotinoids that has been widely used nowadays. Its mode of action is generally by disrupting the post-synaptic acetylcholine receptors (nAChR) upon contact with this insect pest or ingestion. The reaction of imidacloprid is slow, thus, when the insects are exposed to this termiticide, they fail to control their movement, being paralysed and die within few hours (Koehler et al., 2011).

2.4 Imidacloprid, fipronil and bifenthrin

Termiticides such as imidacloprid (chloronicotinyl class), bifenthrin (pyrethroid class) and fipronil (phenyl pyrazole class) are common for controlling subterranean termites with a novel mode of action. Imidacloprid, (1-(6-chloro-3-pyridinylmethyl)-N-nitro-imidazolidin-2-ylideneamine), is a systemic chloronicotinoid termiticide which is used for seeds, soils and foliar applications to control the sucking insects, including rice hoppers, aphids, whiteflies, termites, soil insects, some beetles chewing insects, scales, plant bugs psyllids and various harmful pest species (Bajeer, 2012). It is moderately soluble in water at 20°C. Imidacloprid has the lowest average Koc value (132-310) compared to bifenthrin and fipronil. The half-life of imidacloprid is in the range of 2.01 to 229 days (Rouchaud et al., 1994; Oi, 1999; Sarkar et al., 2001; Fossen, 2006; Sanyal et al., 2006; Anhalt et al., 2008).

Fipronil {5-amino-1-[2, 6-dichloro-4-(trifluoromethyl) phenyl]-4-(trifluoromethyl sulfinyl)-1H-pyrazole-3-carbonitrile} is a broad-spectrum termiticide that is used to control ants, cockroaches, beetles, fleas, ticks, termites, mole crickets, rootworms, weevils and other insect pests. Its water solubility ranges from 1.9 to 2.4 mg/L at 20°C and its Koc value is 803. Fipronil might degrade to its major metabolism to oxidation to sulfone, reduction to sulfide, hydrolysis to amide and photolysis to des-sulfinyl photodegrate (Bobe et al., 1998; Hainzl & Casida, 1996; Ngim & Crosby, 2001; Ying & Kookana, 2002). The half-life ranges from 2 to 342 days (Ngim & Crosby, 2001; Connelly 2001; Ying & Kookana, 2006; Lin et al., 2009a; 2009b; Shuai et al., 2012).

Bifenthrin (2-methyl [1, 1′-biphenyl]-3-yl) methyl, 3-(2-chloro-3, 3, 3-trifluoro-1-propenyl)-2, 2-dimethylcyclopropanecarboxylate) is highly non-polar and lipophilic in nature. It has a solubility of 0.1 mg/L in water and its Koc value is 1.31-3.02 x 10^5. Previous studies have reported that the half-life for field degradation ranges from 122 to 345 days (Fecko, 1999) and up to 13 months (Mulrooney et al., 2006).

2.5 Factors affecting the performance of termiticides

2.5.1 Soil-termiticide interactions

The complexity of soil mixtures containing minerals and organic particles makes it difficult to estimate the influence of termiticides on soil types. When the soil condition is outside of an optimum range, termiticides can be altered to an inactive form, immobilised or absorbed by soils. Effects of organic carbon content and clay on the bioavailability of termites are different within termiticides (Felsot & Lew, 1989; Smith & Rust, 1993; Forschler & Townsend, 1996; Gold et al., 1996; Spomer et al., 2009). The adsorption and desorption of termiticides to the soil are influenced by variations of soil properties such as soil moisture, clay, organic matter content, pH and electrolyte concentration. The physical and chemical properties of termiticides also important for adsorption and desorption of termiticides to the soils (Wiltz, 2012)

2.5.1 (a) Mobility

Termiticide mobility is a significant factor influencing the bioavailability and efficacy of a soil treatment. Termiticide will lose its bioavailability due to the mobility in the soil, making it fail to protect the structure, which at the same time, causing a chemical contamination to the environment contamination (tightly bound to the soil particle). Termiticide mobility is affected by water solubility, pesticide sorption and vapour pressure while by external influences (environment) are weather, soil properties, topography and vegetation.

According to Alley (1993) sorption is an attraction of aqueous species to the solid surface. Several mechanisms influencing the sorption including hydrophobic attraction, ionic attraction and hydrogen bond. The termiticide sorption also can be influenced by pH value especially for a weak acid or based termiticides. Sorption is also affected by soil moisture, texture and organic matter content. The sorption occurs in soil depends mainly on clays and organic matter. Organic matter and clay have a large surface area due to their small particle size, thus, providing high binding site and surface charge. While, sand provides less surface area for binding site (sorption), thus, making termiticides easily leach from the treated areas. Several parameters are applied to describe termiticide sorption in soils (Wiltz, 2012). Table 2.1 shows the sorption parameters for termiticides used in this study.

Table 2.1: Soil sorption parameters of termiticides tested

Termiticide	**KOC (L/kg)**	**Log Kow**	**H2O Solubility (mg/L)**	**Henry's law constant (atmm3 /mol)**	**Reference**
Bifenthrin	1.31 x 105 - 3.02 x 105	6.0	0.1 (25˚C)	7.2 x 10-3	Fecko (1999)
Fipronil	3.8 x 103 – 1.2 x 104	4.01	2.4 (pH 5) 2.2 (pH 9)	3.7 x 10-5	Connelly (2001)
Imidacloprid	1.3 x 102 - 3.1 x 102	0.57	514 (20˚C, pH 7)	6.5 x 10-11	Fossen (2006)

2.5.1 (b) Clay percentage in soil

Soil texture has an important impact on termiticide performance, but the effects differ within termiticides. The clay content in soils was significantly related to termite mortality across all termiticides, application rates, and exposure times (Wiltz, 2010). In assays conducted with bifenthrin, fipronil and chlorfenapyr, *C. formosanus* mortality was the highest when clay content was low (Wiltz, 2010). According to Osbrink & Lax (2002), the mortality of *C. formosanus* workers was higher in the fipronil-treated sand than in treated mixture of soil and clay. Sorption is greatly influenced by the amount of clay and organic matter. Fipronil indicates a significant decrease in adsorption coefficient as the soil clay content decrease, thereby, increasing its bioavailability (Bobé et al., 1997; Cox et al., 1998; 2001). However, an opposite result is shown in some termiticides. Smith & Rust (1993) proved that increased clay content would increase the toxicity of certain pyrethroids such as cypermethrin.

2.5.1 (c) pH

Effects of pH on adsorption and desorption differ with termiticide chemistry and other soil properties. Low pH soils increase the adsorption of weakly acidic termiticide (Halfon et al., 1996; Carrizosa et al., 2000; Boivin et al., 2005). Furthermore, adsorption capability decrease with the increasing pH (Sheng et al., 2005; Ping et al., 2010). In a study by Ping et al. (2010), the adsorption of imidacloprid decreased under higher pH values.

In a soil column experiment, deltamethrin was reported to essentially immobile in three different soils. Kaufman et al., (1981) suggested that the pH may be the main factor affecting the mobility of deltamethrin. In bioassays experiment of treated soils against *C. formosanus*, there was a relation between the effects of soil pH and clay content on the efficiency of chlorfenapyr and fipronil (Wiltz, 2010).

2.5.1 (d) Organic carbon

The termiticide sorption is also influenced by organic carbon content, thus, the partitioning of termiticides between soil organic matter and soil solution affects the bioavailability (Felsot & Lew, 1989). Like clay, organic matter is able to decrease the fipronil adsorption (Bobé et al., 1997). Mulroonei & Gerard (2007) have applied fipronil to three types of soils and found that *R. flavipes* mortality decreased with increased organic carbon. Previous studies also showed that the application of pyrethroid lower than a standard rate was less effective in soils with high organic carbon (Barriuso & Calvet, 1992; Herderson et al., 1998; Worrall et al., 2001; Boivin et al., 2005).

2.5.2 Environmental Factors Affecting Termiticide Degradation

2.5.2 (a) Temperature

Soil temperature affects the termiticide physical and chemical properties. Extreme temperature affects the rate of microbial degradation as the microbial colony unable to survive in extreme conditions. Temperature does have an effect on termiticide adsorption, however, the effects vary among termiticides. Soil temperature is an important factor in termiticide degradation where the adsorption would diminish due to high temperature (Fernández-Bayo et al., 2007). This is particularly true given the facts that temperature had shown its effect on photodegradation and hydrolysis of imidacloprid (Zheng & Liu, 1999; Liu et al., 2006). In their studies, the photodegradation and hydrolysis of imidacloprid notably increased as the temperature increased. A similar observation was made on the half-life of fipronil when this termiticide was reported to decrease when the temperature increased (Ying & Kookana, 2002; Zhu et al., 2004).

2.5.2 (b) Microbial degradation

A microbial degradation is a process of termiticide degradation by microorganisms such as bacteria, fungi and other soil microorganisms as they consume the termiticides as food sources. Numerous studies have indicated that microbes play an important role in pyrethroid degradation in soils (Jordan & Kaufman, 1986; Lee et al., 2004; Gan et al., 2005). According to Sharma & Singh (2012), there was a difference in the half-life of sterile (without microbes) and non-sterile (with microbes) soils for bifenthrin degradation. Non-sterile soil indicated higher bifenthrin degradation compared to sterile soil. A study by Zhu et al. (2004) demonstrated that the half-life of fipronil in non-sterile soil was shorter than in sterile soil. The half-life of fipronil in non-sterile clay loam soil was 8.78 d at 35°C, while, 32.07 d at 35°C in sterile soil. Several termiticide-degrading microbes have been identified includes *Brevibacterium*, *Arthrobacter*, *Corynebacterium*, and *Micromonospora* (De Schrijver & De Mot, 1999).

2.5.2 (c) Photodegradation

Photodegradation is the major termiticide degradation, of which the rate is higher than biodegradation and hydrolysis (Liu et al., 2010). Wamhoff & Schneider (1999) reported that the photodegradation of imidacloprid in pure water, formulated imidacloprid and tap water were 46, 126 and 144 minutes, respectively. These results proved that photolysis occurred rapidly under the UV, even for a short time (Wamhoff & Schneider, 1999). The photodegradation of imidacloprid also increases when the temperature increase (Liu et al., 2006). An experiment done by Husen et al. (2009) indicated that fipronil was stable under the sunlight for one to two weeks after mixing with water. However, within 48 hours of sampling, a significant difference was noted between the sun-exposed sample and the shaded sample (Husen et al., 2009). The degradation of bifenthrin and deltamethrin are also reported to be faster under the UV exposure. The half-life of bifenthrin is believed to be in the range of 99 and 138.6 hours in methanol and acetonitrile under UV irradiation (Tariq et al., 2017).

2.5.2 (d) Hydrolysis

Termiticides also degrade due to hydrolysis (Liu et al., 2010). The hydrolysis of termiticides has received an extensive study because most of the termiticide compounds are contaminants in the environment such as water. The compounds are also adsorbed in lipophilic media. Fipronil, for instance, hydrolyse to an amide as its major metabolites in the aqueous solution (Hainzl & Casida, 1996). According to Husen et al. (2009), fipronil is stable in an aqueous solutions to overcome hydrolysis in mildly acidic to neutral water. Meanwhile, imidacloprid slowly hydrolyse in acidic and neutral water but rapidly in alkaline solutions adjusted to pH 9 (basic condition) with 20% loss after three months (Zheng & Liu, 1999; Liu et al., 2006). According to Zheng & Liu (1999), temperature also influences the hydrolysis process of imidacloprid, thus the rate of hydrolysis increases as the hydrolysis temperature increases (Zheng & Liu, 1999).

2.6 Leaching in soil column

Termiticides need to be persistent in the soil to give continues protection to the building structures or plantations. Excessive applications of termiticides to control subterranean termite can lead to serious environmental contaminations. There are several ways leading to termiticide contaminations to the environment such as precipitation, leaching and dust (Gustafson, 1989; Arias-Estévez et al., 2008; Huseth & Groves, 2014; Delcour et al., 2015). Leaching contributes to the massive contamination that can further lead to underground water contamination (Bajeer, 2012).

The environmental fate of termiticides is mainly controlled by their behaviour in the soil where several physio-chemical and biological processes control their movement and dissipation towards other environmental composition such as air, water and biota (Tang et al., 2012). Knowledge of the termiticide fate is of great concern during its application in the field to prevent a minimum effect on its target and termiticide contamination into the environment. Due to this reason, the leaching behaviour of termiticides is then determined using a soil column method.

Soil column method has been introduced to indicate a transport model (Klein et al., 1997; Butler et al., 1998), for evapotranspiration studies (Prueger et al., 1997; Liu et al., 2002; Sahoo, et al., 2009) and to observe the fate and mobility of contaminants in soil (Jin et al., 1997; Hrapovic et al., 2005; Dontsova et al., 2006). Two types of soil columns have been reported by far, namely a packed column and monolith. The packed column uses disturbed soils where soils are usually dug or disturbed, then, is re-packed into a rigid container and compacted (Bégin et al., 2003; Communar et al., 2004; Hrapovic et al., 2005). The monolith uses undamaged soils from nature and are entirely extracted. Between these two, the packed column is more homogeneous. Several methods are proposed in soil column packing such as dry or damp packing and slurry packing (saturating the soil with water), with the most common method is dry or damp packing. Dry and damp packing methods involve in loading a small amount of dry or damp soil into the container either by hand, spoon or pestle (Lewis & Sjostrom, 2010).

2.7 Termiticide storage

To date, a pest control officer (PCO) or a field biologist in Malaysia frequently mix and apply termiticides in a polyethylene container. The polyethylene container is chosen as it is hard to break compared to a glass container. The container used for termiticide mixing is varied in size and colour but are normally made up of polyethylene. After the mixing, the excess may be placed inside a company vehicle or in a store. The uncovered container placed in the company vehicle may vulnerable to a sunlight as photodegradation is an important factor influencing the degradation of pesticides (Martínez et al., 2009). In contrast, the container placed inside the store may have some protection from the sunlight.

In recent years, there has been an increasing amount of literature on termiticide stability during storage after mixing. To better understand the mechanisms of termiticide degradation in aqueous solution and its effects, Husen et al. (2009) and Spomer et al. (2009) investigated the stability of two most commonly used